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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C07C 17/20, 19/08	A1	(11) International Publication Number: WO 93/25507 (43) International Publication Date: 23 December 1993 (23.12.93)

(21) International Application Number: PCT/US93/05280

(22) International Filing Date: 2 June 1993 (02.06.93)

(30) Priority data:
900,046 17 June 1992 (17.06.92) US

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(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: VAPOR PHASE FLUORINATION PROCESS

(57) Abstract

The present invention relates to a process for the vapor phase fluorination in the presence of a transition metal compound-chromium compound catalyst of a halogen containing no more than three carbon atoms and at least one halogen other than fluorine such that at least one of the halogens other than fluorine is replaced by fluorine. The catalyst comprises a chromium compound and at least one transition metal compound selected from the group consisting of oxides, fluorides, oxyfluorides and acid salts of Ni, Pd and Pt.

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VAPOR PHASE FLUORINATION PROCESS

BACKGROUND OF THE INVENTION

Japanese Patent Application No. 323,688-1988, JA 323,688 (publication No. 172,933-1990) discloses a method of fluorinating 1-chloro-2,2,2-trifluoroethane (HCFC-133a) in the presence of a catalyst which consists of a halogenate or an oxide containing at least one element selected from the group of Al, Mg, Ca, Ba, Sr, Fe, Ni, Co and Mn and Cr.

PCT Application No. WO 89/1034, assigned to Showa Denko discloses a fluorination catalyst made of at least one metal selected from nickel, cobalt, iron, manganese, chromium, copper and silver, and supported on activated alumina. The activated alumina is a critical element of the catalyst which is discussed in detail. The catalyst may be used to catalyze the fluorination of several halohydrocarbons, including the fluorination of HCFC-133(a), perchloroethylene, trichloroethylene and methylene chloride. The examples of the application are for single metal catalysts, and show activity consistent with other prior art.

U.S. Patent No. 4,814,522 discloses a process for exchanging a fluorine atom from one perhaloolefin for a chlorine or bromine atom from another perhaloolefin in the presence of a catalyst selected from the class consisting of chromium oxide alone or in combination with one or more of Rh^0, Ru^0, Ir^0, Pd^0, Pt^0, Ag^0, phosphorus oxide, silicone oxide, boron oxide or an oxide or halide of aluminum, manganese, zinc, iron, rhodium, nickel, palladium, cobalt, platinum, cerium, silver, copper, lead, bismuth, iridium, magnesium, barium, tin, lanthanum, calcium, ruthenium, zirconium, vanadium, molybdenum, or tungsten. HF is not used.

Chromium based catalysts used in the fluorination of

aliphatic haloethanes, and esp cially in the fluorination of HCFC-133a to HFC-134a have unacceptably short lifetimes when used at high pressures where HCl recovery is the most efficient and easiest. To extend catalyst life, the fluorinations are often run at low pressures. However, at low pressures, additional refrigeration is required to recover the HCl byproduct. The added refrigeration requirements also increase the cost of the process equipment. U.K. Patent No. 2,030,981 and Japanese patent application No. 19775-6464 (publication No. 82206 - 1976) disclose introducing air or O_2 into a fluorination reactor to extend catalyst life. However, the introduction of air or O_2 into the reactor has the undesirable effect of oxidizing some of the product thereby decreasing the amount of fluorinated product which is recovered. Furthermore, the loss of product due to the introduction of air or O_2 may increase as the temperature of the fluorination reaction is increased.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process comprising the step of reacting in the vapor phase a halocarbon having three or less carbon atoms, and at least one halogen other than fluorine with anhydrous HF in the presence of a catalyst comprising a chromium compound and at least one transition metal compound selected from the group consisting of oxides, halides, oxyhalides and acid salts of Ni, Pd and Pt at a temperature above 200°C such that at least one of said halogens other than fluorine is replaced by fluorine.

The catalyst material comprises at least one transition metal compound selected from the group

consisting of oxides, halides, oxyhalides and acid salts of Ni, Pd, Pt, and a chromium compound. Where the transition metal is supported on a chromium compound the amount of transition metal is between about 0.1 to about 49 atom % relative to total metal (transition metal and chromium) and preferably between about 0.1 to about 15 atom %. Where the chromium is supported on a transition metal compound the amount of chromium is between about 0.1 to about 49 atom % relative to total metal and preferably between about 0.1 to about 15 atom %.

Where the catalyst material is used with another component (either a binder or a support) the catalyst material comprises between about 10:1 and about 1:10 atom ratio transition metal to chromium. Preferably the atom ratio of the transition metal to chromium is between about 2:1 and 1:2, and most preferably about 1:1. The term catalyst as used herein, includes catalyst material used unsupported, supported or mixed with an appropriate binder.

Any chromium compound may be used, but chromia, Cr_2O_3, and chromium fluoride are preferred. Chromium in the chromium compound may be used in any of its oxidation states, but Cr(III), as the most stable, is preferred. Accordingly, chromia, Cr_2O_3 and CrF_3 are preferred chromium compounds, and chromia and Cr_2O_3 are the most preferred chromium compounds.

Cr_2O_3 may be prepared by any method known in the art, for example, by heating $Cr(OH)_3$ or a chromium oxide gel which has been precipitated from an aqueous solution of Cr(III) compounds by the addition of base; by heating the hydrated chromium oxide gel which results from heating mixtures of urea and aqueous Cr(III) salts; by reacting

CrO_3 with an alcohol or ther suitable reducing agent; by oxidizing an appropriate carbon containing compound such as chromium oxalate or acetate; or by thermal decomposition of a higher oxidation state chromium compound such as $(NH_4)_2Cr_2O_7$ or CrO_3.

The transition metal used is chosen from the elements nickel, palladium and platinum. Preferably the transition metal compound is chosen from metal oxides, hydroxides, halides, oxyhalides and acid salts. More preferably, the transition metal compound is Ni based. Soluble Ni salts and $NiCl_2$ are the most preferred transition metal compounds.

The transition metal compound may be mixed with the chromium compound via any method known in the art such as deposition on the surface of the chromium compound, coextrusion with the chromium compound, coprecipitation with the chromium compound, mixing with other forms of chromium, dispersion throughout a bulk chromium compound or formation of a heterobimetallic compound with chromium. A binder may be added to the catalyst material in any amount up to about 50 weight % of the catalyst to hold the catalyst together. The catalyst may also be formed by simultaneously precipitating the transition metal compound with the chromium compound or the metals may be applied directly onto a catalyst support either sequentially or simultaneously by any of the methods known in the art. Suitable supports are stable in HF or react with HF to form a stable support, and include but are not limited to alumina (Al_2O_3), AlF_3, Al oxyfluoride, Al hydroxyfluoride and carbon. The support comprises at least about 50 weight percent of the catalyst.

Preferably the catalyst material comprises up to about 15 atomic weight percent of the total support and catalyst weight. To improve the catalytic activity and stability of the resulting catalyst, the catalyst may be calcined, either before or after deposition of the transition metal compound.

While the catalysts of the present invention can take any form, powders are not preferred because powders are small enough to be carried through the reactor or cause large pressure drops. Accordingly, the catalysts of the present invention are preferably shaped. The catalysts may be prepared in any shape, and by any technique known in the art such as extrusion or tableting. Catalysts may also be formed into large chunks, spheres or any other convenient shape.

The catalyst may be dried before use. The resulting catalyst may be pretreated in the reactor by passing anhydrous HF over the catalyst. It is believed that the anhydrous HF fluorinates some of the catalytic material and possibly the support (if one is used). Under reaction conditions the exact structure and composition of the catalyst surface may be quite complex. The catalyst may exist as mixtures of chromium and transition metal oxides, halides, oxyhalides, acid salts and/or other compounds depending on the starting materials. Whatever the actual structure of the catalyst when in use, the term catalyst includes such oxides, halides, oxyhalides and/or acid salts and their derivatives.

The resulting catalyst is useful in the fluorination of a halocarbon containing no more than 3 carbons and at least one halogen other than fluorine such that at least

one of the halogens other than fluorine is replaced by fluorine. Suitable halocarbons are saturated or unsaturated and partially or fully halogenated. Preferred halocarbons include methylene chloride, CCl_2CCl_2 (PCE), $CHCl_2CF_3$ (HCFC-123), $CHClFCF_3$ (HCFC-124), $CHClCCl_2$ (TCE), and CH_2ClCF_3 (HCFC-133a). More preferably the halocarbon is selected from 1-chloro-2,2,2-trifluoroethane (HCFC 133a), CCl_2CCl_2, and $CHClCCl_2$.

The fluorination is conducted in a reactor made of corrosion resistant material, such as Inconel. The reactor is charged with the catalyst, and heated to the reaction temperature by any suitable method, such as placing the reactor in a furnace, salt or sand bath. The reaction temperature depends upon the particular halocarbon being fluorinated, and is preferably between about 200°C and about 550°C. However, a benefit of the present catalyst is that its catalytic activity is not impaired when used in fluorination reactions at high temperatures, those greater than about 300°C. Accordingly, the addition of air or oxygen is not required. For example, temperatures between about 325°C and about 450°C are preferred for the fluorination of 1-chloro-2,2,2-trifluoroethane.

While the addition of oxygen or air is not required, a small quantity of oxygen or air may be added to the fluorination reaction to further increase the life of the catalysts of the present invention. The amount of oxygen or air which is added is preferably between about 0.01 to about 10 mole % O_2 or air per mol of halocarbon to be fluorinated.

The reaction may be conducted at any pressure from

sub-atmospheric to super-atmospheric pressures. However, one of the primary benefits of the catalysts of the present invention is their catalytic longevity. Accordingly, catalysts of the present invention may be used at pressures up to about 300 psi.

To insure the optimum yield, and to prevent corrosion of the equipment, the fluorination is carried out under anhydrous conditions. While up to about 10,000 ppm H_2O may be present in a commercial reactor, water in such amounts causes unacceptably high corrosion of the equipment. Accordingly, under commercial conditions the amount of water present is preferably less than about 6,000 ppm and most preferably below about 2,000 ppm. On a laboratory scale the amount of H_2O is preferably less than about 300 ppm. Catalyst may be dried via heating in any gas which does not react with the catalyst, and preferably N_2. The catalyst may then be pretreated in the reactor by flowing anhydrous N_2/HF through the catalyst bed.

HF and halocarbon are pumped into the reactor at a rate sufficient to insure adequate contact times preferably between about 0.1 and 100 seconds, and more preferably between about 1 to about 40 seconds.

The effluent from the reactor is removed and the desired fluorinated halocarbon may be isolated from the effluent via any conventional means. All percents expressed in the examples are mole percent.

EXAMPLE 1

A catalyst was made by impregnating 50.0 gm of 1/16" (1.6 mm) Cr_2O_3 extrudate with a solution of 6.18 gm $NiCl_2 \bullet 6H_2O$ in 150 mL of deionized water. After 2 hours,

the water was removed and the sample was dried, yielding a catalyst containing 3.6% nickel.

An Inconel reactor (0.3 inch ID, 25 inch long tube) was charged with 18.0 cc of catalyst and placed in a sand bath. The reactor was heated to 400°C over approximately 4 hours, and a flow of nitrogen was passed through the catalyst bed. Nitrogen was bubbled through HF at a pressure of 200 psi (1.38×10^3 kPa). The catalyst was then subjected to a flowing N_2/HF stream for 3.5 hours.

After this pretreatment a feed consisting of 5:1 mole ratio of HF:1,1,1-trifluorochloroethane was pumped into the reactor at sufficient flow so as to maintain a 10 second contact time at 400°C and 200 psi. Analysis of the reactor effluent was performed by an on-line gas chromatograph. The results are shown in Table 1. The percent of HCFC-133a which is fluorinated (moles HCFC-133a fluorinated/moles HCFC-133a throughput) is listed under Conversion. Selectivity is percent of the moles of a fluorination product divided by the moles of HCFC-133a converted. HFC-134a (CF_3CFH_2) is the desired product.

TABLE 1

Time	Conversion CF_3CClH_2	Selectivity CF_3CFH_2	CF_3CH_3	CF_3CHFCl
10 hrs	39.1%	82.5%	16.2%	0.8%
20 hrs	33.3%	83.6%	14.5%	1.4%
30 hrs	41.4%	79.0%	19.9%	1.0%
40 hrs	38.6%	78.1%	20.7%	1.1%
50 hrs	26.8%	80.9%	17.3%	1.6%
60 hrs	21.8%	84.1%	13.8%	1.7%
Average	33.5%	81.4%	17.1%	1.3%

The rate of conversion remained high over the entire reaction showing a 21.8% conversion rate after 60 hours. Selectivity for the CF_3CFH_2 remained high throughout the fluorination.

EXAMPLE 2

A supported NiCr catalyst was prepared by cofeeding an aqueous solution (38 ml) containing 4.22 gm $NiCl_2 \cdot 6\ H_2O$ and 2.00 gm CrO_3 with 19 ml methanol onto 32.69 gm of partially fluorinated alumina spheres (3 mm diameter). The excess liquid was evacuated at 70°C and the solid was dried at 125°C for 16 hours. The resulting catalyst contained 3% nickel and 3% chromium (Ni/Cr mole ratio = 0.9).

An Inconel reactor having an ID of 0.6 inches (1.5 cm) and a length of 25 inches (63.5 cm) was charged with 20.0 cc of catalyst and placed in a sand bath. The reactor was heated to 375°C over approximately 4 hours and held for an additional 6 hours. Nitrogen was passed over the catalyst at a rate of 450 cc/min. The temperature was reduced to 200°C and nitrogen was bubbled through HF at atmospheric pressure. The temperature was raised to 350°C after one hour. A stream of HF/N_2 was passed over the catalyst for 4 hours.

A 4:1 HF:1,1,1-trifluorochloroethane was pumped into the reactor at 50 psig and 350°C at rates sufficient to insure the contact times listed in Table 2, below. Air was added at a rate sufficient to ensure an oxygen:1,1,1-trifluorochloroethane mole ratio of 0.015. Analysis of the reactor effluent was performed by an on-line gas chromatograph. The results are shown in Table 2.

Table 2

Contact Time	10.1 sec	4.5 sec	2.2 sec
CF_3CClH_2 Conversion	21.8%	16.2%	10.9%
CF_3CFH_2 Selectivity	97.3%	95.5%	92.8%
CF_3CFH_2 Productivity (lb/h/cu.ft.)	8.0	16.6	21.3

The rate of conversion and productivity for CF_3CFH_2 remained high even at commercially preferred, low contact times.

EXAMPLE 3

A NiCr/AlF_3 catalyst made according to Example 2 was loaded into the Inconel reactor and dried at 400°C for 4 hours. It was then treated with HF at 400°C for 4 hours and cooled to 290°C. HF and CCl_2CCl_2 were passed through the reaction under the conditions shown across the first row of Table 3. After 130 hours the temperature was raised to 310°C. The reaction products, selectivity and productivity at both temperatures are shown in Table 3.

TABLE 3

HF:PCE=8:1, 100 psig, 300°C, 20 sec. contact time		
	Selectivity (%)	
Species	@300°C	@310°C
CHF_2CF_3	0	0.1
CHF_2CClF_2	0.2	0.3
$CHClFCF_3$	3.4	5.7
$CHClFCClF_2$	7.5	7.3
$CHCl_2CF_3$	53.6	58.3
$CHCl_2CClF_2$	26.0	18.3
$CHCl_2CCl_2F$	0.6	0.4
$CClFCCl_2$	7.2	7.4

The selectivity displayed for $CHCl_2CF_3$ at both temperatures is good.

EXAMPLES 4-6

The $NiCr/AlF_3$ catalyst prepared in Example 2 is loaded into a Inconel reactor, dried and heated as in Example 2. The organic compounds listed in Table 4 are passed over the catalyst under the conditions listed in Table 4.

TABLE 4

organic compound	HF:org.	T(°C)	P(Psig)	Res. time
$CHClFCF_3$	4:1	320	75	12
$CHClCCl_2$	13:1	325	200	12
CH_2Cl_2	4:1	275	50	16

The primary products are list d in Table 5 b low.

TABLE 5

organic	Primary Product
$CHClFCF_3$	$CHClFCF_3$ + CHF_2CF_3
$CHClCCl_2$	CH_2ClCF_3
CH_2Cl_2	CH_2F_2

COMPARATIVE EXAMPLE 1

The Cr_2O_3 used in Example 1 was subjected to the same water treatment used to impregnate the catalyst of Example 1, except that no nickel was added. The same reaction conditions were also employed. The results are shown in Table 6.

TABLE 6

Time	Conversion CF_3CClH_2	Selectivity CF_3CFH_2	CF_3CH_3	CF_3CHFCl
10 hrs	20.2%	88.3%	10.3%	1.3%
20 hrs	13.4%	88.6%	9.9%	1.4%
30 hrs	7.3%	88.1%	10.4%	1.3%
40 hrs	4.62%	87.2%	10.8%	1.6%
50 hrs	3.2%	86.4%	11.1%	1.9%
60 hrs	2.6%	86.3%	11.4%	1.8%
Average	8.6%	87.4%	10.6%	1.6%

The rate of conversion was much lower (one fourth) than that displayed by the catalyst of the present invention (Example 1), and decreased sharply at 30 hours. The decrease over time of the rate of conversion of HCFC-133a indicates a short catalyst life.

COMPARATIVE EXAMPLE 2

A catalyst consisting of nickel supported on gamma alumina extrudate was prepared by impregnating 40 gm alumina with an aqueous solution containing 4.94 gm

$NiCl_2 \cdot 6H_2O$. The water was removed and the catalyst dried at 145°C for 16 hours. The catalyst was pretreated as in Example 1 and was run at 400°C for the first 20 hours. The temperature was then increased to 425°C for the remainder of the experiment. The results are shown in Table 7.

TABLE 7

Time	Conversion CF_3CClH_2	Selectivity CF_3CFH_2	CF_3CH_3	CF_3CHFCl
10 hrs	3.4%	90.6%	1.7%	3.9%
20 hrs	3.2%	92.4%	1.6%	2.1%
30 hrs	6.9%	95.6%	1.5%	0.7%
40 hrs	7.6%	96.0%	1.3%	1.2%
50 hrs	7.3%	96.4%	1.2%	0.8%
60 hrs	6.6%	96.5%	1.2%	0.6%
Ave (400°)	3.3%	91.5%	1.6%	3.0%
Ave (425°)	7.1%	96.1%	1.3%	0.8%

The NiCr catalyst of the present invention displayed an average conversion of 33.5%, and an average selectivity for HFC-134a of 81.4% over the first 60 hours. Thus, the catalysts of the present invention convert ten times as much of the HCFC-133a starting material compared to Ni alone on alumina and about three times better than bulk Cr_2O_3.

Comparing the results of the examples, the Cr_2O_3 supported nickel catalyst of Example 1 has a longer life and higher conversion of HCFC-133(a) than does Cr_2O_3 used alone at the same temperature (Comparative Example 1). Finally, the results of Comparative Example 2 indicate that a nickel catalyst supported on alumina and containing no chromium displays a much lower conversion of HCFC-133(a) CF_3CClH_2 than does nickel on chromia.

There therefore exists a synergistic effect between nickel and chromium compounds which makes catalyst containing both nickel and chromium compounds better catalysts for fluorination reactions than either chromium compounds alone, or nickel compounds supported on a substrate without chromium compounds.

COMPARATIVE EXAMPLES 3-9

The following examples compare four catalysts; MgCrAl, FeCr and MnCr with NiCr catalysts disclosed in JA 322,688. MgCrAl-oxide was chosen because it displayed the best catalytic activity of the catalysts prepared in JA 323,688. FeCr-oxide was chosen because it was the only mixed metal catalyst containing Cr and a transition metal prepared in JA 323,688. MnCr-oxide was chosen for comparison (even though it was not prepared in JA 323,688) as it is also a mixed metal catalyst containing Cr and a transition metal. The MgCrAl-oxide and FeCr-oxide catalysts were prepared according to the examples given in JA 323,688. The MnCr-oxide and NiCr-oxide catalysts were prepared as close to the disclosure of JA 323,688 as possible, and differences are noted.

COMPARATIVE EXAMPLE 3

"MgCrAl-Oxide" catalyst. This catalyst was prepared exactly as described in JA 323,688. 1100 g $Al(NO_3)_3 \cdot 9H_2O$, 125 g $Cr(NO_3)_3 \cdot 9H_2O$ and 40 g $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved in 2.5 l of water. 2000 g of 28% ammonium hydroxide was added, with stirring. The mixture was added to 4 l of heated water (80°C). The resulting precipitate was filtered, washed with deionized water and dried at 125°C for 16 hours. The dried catalyst was baked at 450°C for 5 hours. After drying the catalyst was in "chunks".

pieces which were about 5mm in size were used. The mole ratios were: Al/Cr=9.4, Mg/Cr=0.5.

COMPARATIVE EXAMPLE 4

"FeCr-Oxide" catalyst. This catalyst was prepared via the procedure described above (which is exactly as in JA 323,688, Example 5), except that 800 g $Fe(NO_3)_3 \cdot 9H_2O$ and 198 g $Cr(NO_3)_3 \cdot 9H_2O$ were used ($Fe(NO_3)_2 \cdot 9H_2O$ was specified by JA 323,688, but was not available, and was found not to be stable). The mole ratio was: Fe/Cr=4.0.

COMPARATIVE EXAMPLE 5

"MnCr-Oxide" catalyst. Preparation of this catalyst was not described in JA 323,688, so the preparation and mole ratio (4.0) used for the FeCr catalyst were used to make the MnCr catalysts, except that 377 g $Mn(NO_3)_2 \cdot 4H_2O$ and 150 g $Cr(NO_3)_3 \cdot 9H_2O$ were used.

COMPARATIVE EXAMPLE 6

"NiCr-Oxides" catalyst. This catalyst was also not specifically described or prepared in JA 323,688, and cannot be synthesized by the above procedure due to the solubility of Ni in the ammonia solution which is used to precipitate out the metal hydroxide. Thus, 323 g $Ni(NO_3)_2$ 6 H_2O and 500 g $Cr(NO_3)_3$ $9H_2O$ were mixed in 2.5 l of water. To remain as close to JA 323,688 as possible, the mixture was heated to 80°C and then allowed to age at room temperature for 24 hours to precipitate the Ni hydroxides. Some of the Ni was washed away, so the final Ni/Cr ratio was somewhat less than 1. The catalyst was dried and baked as above.

COMPARATIVE EXAMPLE 7

Each of the catalysts prepared in Comparative Examples 3 through 6, were screened in a reactor under

conditions that were chosen to duplicate th conditions specified in JA 323,688. Approximately 95 ml of catalyst was charged to an Inconel 600 reactor and dried at 375°C for eight hours with nitrogen flowing over the catalyst at 200 ml/min. The temperature was decreased to 200°C, after which time nitrogen was bubbled through a cylinder containing HF so that the nitrogen stream (200 ml/min) contained HF to pretreat the catalyst. This procedure lasted four hours, during which time the temperature was increased to 350°C. At this point, the nitrogen/HF stream was stopped, and the reaction was started. The HF and HCFC-133a reactants were premixed at a mole ratio of 3:1 (HF:HCFC-133a). The premixed reactants were fed over the catalyst at a rate of 185 ml/min., and air was fed at a rate of 4.9 ml/min at atmospheric pressure. Each catalyst was used for two weeks. These conditions equate to the same contact time (30 seconds), O_2:HCFC-133a mole ratio and HF:HCFC-133a mole ratio as described in JA 323,688. The results (% starting material converted, selectivity of conversion to 134a, productivity, and % converted to 134a are shown in Table 8.

TABLE 8				
350°C, 0 psig, 30 sec contact time, 0.02 O_2:133a, 3:1 HF:133a				
catalyst (prepared in)	NiCr- (CE6)	MgCrAl (CE3)	MnCr- (CE5)	FeCr- (CE4)
133a conversion	21%	16%	>26%	12%
134a selectivity	93%	93%	<59%	45%
134a productivity (lb/h/cu.ft)	0.7	0.5	0.6	0.2
conversion to 134a	19.5%	15%	15%	5.4%

These values represent averages after all reaction conditions stabilized and the catalyst showed stable performance. It is typical for the conversions to be high at the beginning of the test and then to quickly drop to a more stable value. Thus, the results reported in Table 8 are best compared to the results after 6 months reported in JA 323,688. The MgCrAl-oxide catalyst produced in Comparative Example 3 duplicated the results reported in JA 323,688 well (18% 133a converted, 94% selectivity for 134a, 17% converted to 134a). The FeCr-oxide catalyst shows slightly poorer performance than what is reported in JA 323,688 (10% 133a converted, with 80% selectivity for 134a, and 8% converted to 134a). The MnCr-oxide catalyst displayed activity between the MgCrAl-oxide and the FeCr-oxide catalysts (no example was reported in JA 323,688). The NiCr-oxide catalyst

displayed slightly better performanc than the oth r catalysts at the conditions of this Example. However, the slow flow rates of the reactants across the catalyst bed result in a relatively long contact time for the fluorination reaction, which results in low productivity, and is accordingly not preferred. As a result, the reactants have more time to react, and the differences between even widely varying catalysts becomes narrow and difficult to differentiate. The relative quality of various catalysts is apparent under more rigorous, commercially preferred, conditions such as those employed in Comparative Example 8 and 9, below.

COMPARATIVE EXAMPLE 8

The fluorination reaction of 133a to 134a using the MnCr-oxide was continued as above, except that the flow rate of 133a was increased so that the contact time was 13 seconds. All other conditions were the same as above. The conversion rate of 133a dropped to 5%, and the selectivity of 133a which was converted to 134a was less than 78%.

COMPARATIVE EXAMPLE 9

Fluorinations using each catalyst (except MnCr) were run under the conditions suitable for commercial fluorination, which are listed across the first row of Table 9. These conditions are more desireable for commercial fluorination. The results are shown in Table 9, below.

TABLE 9

350°C, 50 psig, 10 sec contact time, 0.015 oxygen:133a, 4:1 HF:133a

catalyst (prepared in)	NiCr (CEx6)	MgCrAl (CEx.3)	FeCr (CEx4)
133a conversion	21%	4%	2%
134a selectivity	95%	76%	70%
134a productivity (lb/h/cu.ft)	6.4	1.3	1.0
conversion to 133a	20%	3%	1%

The conversion rates of the MgCrAl-Oxides and FeCr-Oxides dropped dramatically at higher pressure and lower contact time (from 16% and 12% respectively, to 4% and 2% respectively). However, the conversion rates for the NiCr-oxide remained constant at 21% and the selectivity increased slightly. Thus, the NiCr catalyst display vastly improved productivity of HFC 134a, which is at least ten times greater than any of catalysts made according to JA 323,688. Thus, the NiCr catalyst displays activity at commercial conditions which is markedly better than the "best" catalyst compositions produced in the examples of JA 323,688. The surprising activity at commercial conditions of NiCr catalyst could not have been predicted from the compositions and fluorination conditions which are disclosed in JA 323,688. Moreover, the prior art catalyst compositions displaying the best activity contain Mg, an alkaline

earth, not a transition metal. Thus, JA 323,688 neith r recognized nor suggested the surprising catalytic activity of the NiCr catalysts.

We Claim:

1. A fluorination process comprising the step of: reacting in the vapor phase a first halocarbon having three or less carbon atoms, and at least one halogen other than fluorine with anhydrous HF in the presence of a catalyst comprising at least one transition metal compound selected from the group consisting of oxides, halides and oxyhalides of Ni, Pd and Pt and a chromium compound at a temperature above 200°C to produce a second halocarbon wherein at least one of said halogens other than fluorine is replaced by fluorine.

2. The process of claim 1 wherein said catalyst is either supported or mixed with a binder and said transition metal and said chromium compound are present in a transition metal to chromium atomic ratio between about 10:1 and about 1:10.

3. The process of claim 2 wherein said catalyst support is chosen from the group comprising Al_2O_3, AlF_3, Al oxyfluoride, Al hydroxyfluoride and carbon.

4. The process of claim 3 wherein said chromium compound is selected from chromia, Cr_2O_3, CrF_3, or chromium oxyfluoride.

5. The process of claim 4 wherein said first halocarbon is selected from the group consisting of methylene chloride, CCl_2CCl_2, $CHCl_2CF_3$, $CHClFCF_3$, $CHClCCl_2$, and CH_2ClCF_3.

6. The process of claim 4 wherein the first halocarbon is CH_2ClCF_3, and the second halocarbon is CF_3CH_2F.

7. The process of claim 4 wherein the first halocarbon is CCl_2CCl_2, and the second halocarbon is $CHCl_2CF_3$.

8. The process of claim 4 wherein the first halocarbon is $CHClCCl_2$, and the second halocarbon is CH_2ClCF_3.

9. The process of claim 1 further comprising the step of introducing O_2 or air to said fluorination process.

10. The process of claim 2 further comprising the step of introducing O_2 or air to said fluorination process.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/05280

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07C17/20; C07C19/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category°	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
P,X	EP,A,0 516 000 (DAIKIN INDUSTRIES) 2 December 1992 see page 2, line 46 - page 3, line 56; claims; example 4 ---	1-6
X	EP,A,0 486 333 (ELF ATOCHEM) 20 May 1992 see the whole document ---	1-6,9-10
A	FR,A,2 433 500 (DAIKIN) 14 March 1980 see the whole document -----	1-10

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
26 AUGUST 1993	- 6. 09. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	ZERVAS B.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9305280 SA 75137

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 26/08/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		AU-A-	8779991	14-05-92
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82